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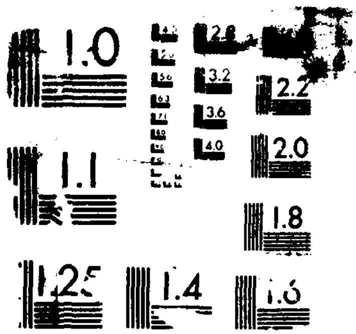

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Application of XAD-4 Solid Sorbent to the Collection of Pesticides from Water Samples

Final Report

M. P. Maskarinec
D. L. Manning

Supported by

U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, Maryland 21010-5401

Project Officer: Mary Ann Ryan

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This report summarizes work done to evaluate the efficiency of XAD-4 resin for removing pesticides from water for subsequent analysis. A limited number of pesticides, including lindane, aldrin, and 4,4'-DDT, were added to water, extracted by elution on XAD-4, and analyzed by gas chromatography with electron capture detection. The method was found to be reasonably effective, at least for semiquantitative purposes.

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Application of XAD-4 Solid Sorbent to the Collection of Pesticides from Water Samples

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EXECUTIVE SUMMARY

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is supporting collection and analytical methods development in support of the Installation Restoration Program. One of these development efforts involves the use of sorbent tubes for the isolation of contaminants from water. Collection of the sample on a sorbent tube has the advantages of increased stability and reduced shipping cost for the sample.

This report describes experiments performed in order to assess the applicability of XAD-4 resin columns for the collection of pesticides from water. Lindane, aldrin, and 4,4'-DDT were added to water and collected on XAD-4. The pesticides were eluted form the resin using acetone. The analysis was carried out by gas chromatography with electron capture detection. The procedure was tested over the range of 5-100 μg/L.

Recoveries of the three pesticides varied with the individual compound. Lindane was recovered at higher percentages than aldrin and 4,4'-DDT, which were recovered at similar levels. Even single compounds showed variability in the recovery over the range tested. The methodology is effective for the determination of these compounds, at least semiquantitatively.

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INTRODUCTION

As a general class of compounds, pesticides have been arguably the most widely studied from an environmental standpoint. This has been due to early recognition of adverse effects on the environment from pesticide usage. As a result, the environmental literature is replete with examples of methodology for the determination of various pesticides in environmental samples. The USEPA has promulgated several methods for the determination of these compounds. These methods are quite similar, varying only in their applicability to particular matrices. Water samples are extracted with organic solvent, the extract is dried and concentrated, and analysis is carried by injection of an aliquot of the concentrate into a gas chromatograph equipped with an electron capture detector. This general approach is certainly the most widely used, but requires shipment of large volumes of water to the laboratory. In the case of the pesticides, a separate sample is often used, doubling the volume required if other semivolatile organics are to be analyzed. An additional problem is that the pesticides are not very soluble in water, and are therefore not completely stable after sampling.

Previous work had identified XAD-4 resin as useful for the collection of explosive compounds from water. If the method could be extended to other semivolatile organics, such as pesticides, the extract from the cartridge could be used for screening purposes in preliminary site investigations or remedial actions. This would greatly reduce the volume of sample shipped to the analytical laboratory and perhaps improve the stability of the compounds. This report focuses on the performance of that methodology for the determination of lindane, aldrin, and 4,4'-DDT.

EXPERIMENTAL

Preparation of XAD-4 Columns

The bulk XAD-4 is precleaned by Soxhlet extraction with acetone for 48 hours. The Soxhlet extractor is operated in the normal manner. At the conclusion of the Soxhlet extraction, the acetone is drained from the extractor and replaced with methanol. After the initial Soxhlet extraction is completed, <u>the resin is never allowed to dry out</u>. The cleaned resin is stored in an Erlenmeyer flask under methanol until the collection columns are filled.

The cartridges, (1/4" x 10" glass tubes) are cleaned by rinsing with methanol. A glass wool plug is inserted in one end of the tube and a capped union is attached. The tube is filled with methanol and all bubbles are removed. A slurry of XAD-4 in methanol is then added, and the methanol is allowed to drain slowly from the tube by loosening the union cap. When sufficient resin has been added to bring the level to within 1/4" of the filling end of the tube, a second glass wool plug is inserted and the tube ends are capped. The capping was accomplished by submerging the tubes in methanol.

Collection of Water Samples

For collection of the samples, the tubes are uncapped and 25 mL of pesticide grade water are pumped through the column to remove the methanol. The sample is placed in a volumetric flask of 100 mL volume. The volume used depends on the expected level of pesticide in the sample and the ultimate detection limit required. Teflon tubing (1/8") is used to siphon the water sample through the columns by gravity flow. The flow rate should be 3-6 mL/min. The entire sample is allowed to drain through the column. Again, the column is not allowed to go dry. Ten mL of pesticide grade water is added to the column after the sample has been collected; the tube is capped; and the column is refrigerated to 4°C prior to shipping and/or analysis.

The tubes are desorbed by passing acetone through the column at a rate of 3-6 mL/min. Three to five drops of water are allowed to drain from the column, and the next 10 mL are collected for analysis. This acetone extract represents the final solution for analysis. For certain analytical methods, it may be prudent to add 1 g anhydrous sodium sulfate to remove all traces of water. If necessary, the extract can be further concentrated prior to analysis.

Gas Chromatographic Analysis

The results reported here were obtained using gas chromatography with electron capture detection. A Perkin-Elmer Sigma 300 gas chromatograph was used. The instrument was equipped with a Model AS-300 autosampler and an electron capture detector. The splitless injection techniques was used, and the column was a 30 M x 0.25 mm DB-5 fused silica capillary column. The calibration was by the method of external standards using a 5 point calibration curve. The results were recorded using a Hewlett-Packard Model 3390A integrator. A representative chromatogram is shown in Figure 1.

RESULTS AND DISCUSSION

From an analytical standpoint, solid phase extraction methods require: 1) adequate sorption efficiency of the compounds of interest, 2) adequate recovery of the compounds from the sorbent, and 3) adequate clean-up of the sorbent for the purpose of the final measurement method. In the case of the pesticides, clean-up was expected to provide the major obstacle to successful use of the sorbent. Previous attempts to analyze explosives indicated that substantial interference was noted when using gas chromatography with electron capture detection. However, the clean-up techniques described here, combined with the use of the capillary column, produced blank chromatograms which contained no interfering peaks. The use of pesticide grade water is also probably necessary for the maintenance of clean background.

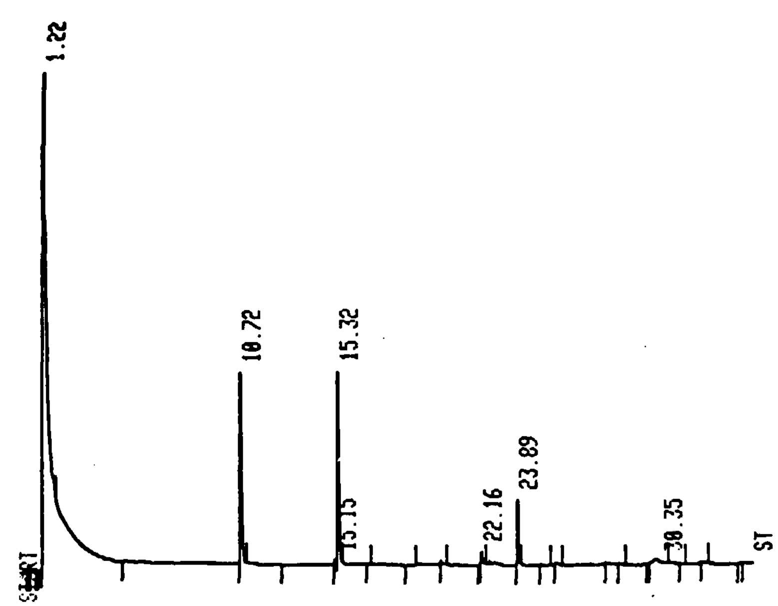

Figure 1. Separation of Pesticides by gas chromatography with electron capture detection.

RT	Pesticide
10.72	Lindane
15.32	Aldrin
23.89	4,4'-DDT

The sorption efficiency of the resin for pesticides was evaluated by use of a backup column on the high level samples. No pesticides were ever found on the backup column. Therefore, it was concluded that the XAD-4 resin was suitable for the collection of these compounds, in terms of capacity. Because of the limited solubility of the pesticides in water, and the hydrophobic nature of the interaction with the resin, it is likely that even highly contaminated samples could be effectively extracted using the resin.

Overall extraction efficiency results are shown in Tables 1-4. Recovery of lindane was greater than the recovery of either of the other analytes, and all of the analytes were best recovered at the lowest level and at the highest level. The reason for this behavior is unclear, although it can be speculated that the addition of these compounds to a water matrix produces unreliable actual concentrations. At the lowest level, the compounds are most soluble, with lindane having the highest solubility. At higher levels, processes such as adsorption onto the container walls can have a marked effect on the actual concentration of the pesticide in the water. At even higher levels, the pesticides may not be in solution at all, but may be carried as precipitates through the resin column, which simply acts as a filter. In this situation, solvent extraction would seem to have an advantage, in that the container walls can be rinsed with the solvent, and the separatory funnel walls come into intimate contact with the solvent. If the resin technique is to be useful, the same techniques should be used; the container could be rinsed with the eluting solvent and all subsequent surfaces should be brought into contact with that solvent.

In spite of these difficulties, the resin is reasonably effective in terms of collecting these compounds and providing an extract suitable for analysis according to accepted methods. Further refinement of the method could result in a quantitative extraction technique with all the attendant advantages of solid phase extraction.

APPENDIX

PROCEDURE FOR THE COLLECTION OF PESTICIDES FORM WATER FOR ARCHIVAL STORAGE AND SEMI-QUANTITATIVE ANALYSIS

1. Application

This method is applicable to ground and surface water and is suitable for the preservation of samples for future analysis. The method has been validated for Lindane, Aldrin, and 4,4'-DDT.

a. Tested Concentration Range: (μg/L)

Lindane:	5-100
Aldrin:	5-100
4,4'-DDT:	5-100

b. Sensitivity: The sensitivity of this method is dependent on the concentration factor. A 100 mL sample concentrated to 10 mL gives a concentration factor of 10. Thus, the sensitivity is 10 times lower than that of the analytical method.

c. Detection Limit: (μg/L)

Lindane:	10
Aldrin:	10
4,4'-DDT:	10

d. Collection Rate: The collection of a 100 mL sample requires approximately one hour. Any number of samples can be extracted simultaneously.

e. Measurement Procedure: Any approved analytical method can be applied to the measurement of the pesticides in the collected extract. The data presented here are the result of measurement by GC with electron capture detection.

2. Apparatus

a. Hardware:

Constant-flow pump capable of 15 mL/min at 30 psig
1/4" teflon tubing, 2'
1/8" teflon tubing, 3'
1/4 to 1/8 reducing union
1/4 to 1/4 reducing union

b. Glassware:

1/4" borosilicate glass tubes, 10" in length
Soxhlet extractor, 200 mL capacity
Erlenmeyer flask, 1 L
Volumetric flask, 50-100 mL (1/sample)
Centrifuge tubes, 15 mL, screw-capped (1/sample)
Pyrex wool

c. Chemicals:

Methanol, distilled-in-glass grade
Acetone, distilled-in-glass grade
Water, organic-free
Lindane
Aldrin
4,4'-DDT
Other pesticides as required
XAD-4, 20-60 mesh

3. Standards: Concentrated stock solutions of Lindane, Aldrin, and 4,4'-DDT were prepared by dissolving 100 mg of the pure material in 100 mL of pure methanol. Solutions were stored at 4°C.

Stock solution A containing a mixture of lindane, aldrin, and 4,4'-DDT at a concentration of 100 μg/mL were prepared by adding 10 mL each of the concentrated stock solutions to a 100 mL volumetric flask and diluting with methanol.

Solutions for recovery studies at multiples of detection limit (DL) were prepared from the standard solutions as follows:

10 DL: 50 μL of stock solution A to 50 mL water. Calibration standard in 5 mL acetone.

5 DL: 25 μL stock solution A to 50 mL water. Calibration standards in 5 mL acetone.

2 DL: 10 μL of stock solution A to 50 mL water. Calibration standards in 5 mL acetone.

1 DL: 10 μL of stock solution A to 50 mL water. Calibration standards in 5 mL acetone.

0.05 DL: 5 μL of stock solution A to 100 mL water. Calibration standards in 5 mL acetone.

4. Procedure:

The XAD-4 resin to be used is precleaned by Soxhlet extraction with acetone for 48 hours. The Soxhlet extractor is operated in the normal manner. At the conclusion of the Soxhlet extraction, the acetone is drained from the resin and replaced with methanol. After the Soxhlet extraction, the resin is never allowed to dry out. The cleaned resin is stored in an Erlenmeyer flask under methanol until the collection cartridges are filled.

The cartridges (1/4" x 10" glass tubes) are cleaned by rinsing with methanol. A glass wool plug is inserted in one end of the tube and a capped union is attached. The tube is filled with methanol and all air bubbles removed. A slurry of XAD-4 in methanol is then added, and the methanol is allowed to drain slowly from the cartridge by loosening the union cap. When sufficient resin has been added to bring the level within 1/4" of the top of the tube, a second glass wool plug is inserted and the ends are capped. The capping can be accomplished using capped unions or, more economically, by submerging the tube in methanol.

For collection of the sample, the tubes are uncapped and 25 mL of organic-free water are pumped through the column in order to remove the methanol. The sample is placed in a volumetric flask of 100 mL volume (smaller volumes can be used if the levels of pesticides are expected to be high). Teflon tubing (1/8") is used to siphon the water sample through the resin cartridge by gravity flow. The flow rate should be adjusted to 3-6 mL/min. The entire sample is allowed to drain through the cartridge. Again, the cartridge is not allowed to go dry. Ten mL of organic-free water is added to the tube after the sample has been collected; the tube is capped; and refrigerated at 4°C prior to analysis.

The tubes are desorbed by passing acetone through the tube at a rate of 3-6 mL/min. Three to five drops of water are allowed to drain from the tube, and the next 10 mL are collected for analysis. This acetone extract is the final sample for measurement of the pesticides.

Table 1 - Replicate 1 Data

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
Lindane	5	4.6	93
	10	6.2	62
	20	9.6	48
	50	30	60
	100	74	74
Aldrin	5	2.9	57
	10	4.5	45
	20	7.2	36
	50	24.5	49
	100	66	66
4,4'-DDT	5	4.3	86
	10	5.0	50
	20	11	56
	50	27	54
	100	84	84

Table 2 - Replicate 2 Data

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
Lindane	5	4.8	96
	10	6.5	65
	20	12.0	60
	50	30.0	60
	100	76	76
Aldrin	5	3.3	65
	10	4.7	47
	20	8.6	43
	50	26.0	52
	100	68.0	68
4,4'-DDT	5	3.1	62
	10	4.2	42
	20	12.0	60
	50	32.0	64
	100	78.0	78

Table 3 - Replicate 3 Data

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
Lindane	5	4.7	93
	10	5.1	51
	20	12.0	60
	50	32.0	63
	100	77.0	77
Aldrin	5	2.7	54
	10	3.6	36
	20	9.2	46
	50	28.0	55
	100	75.0	75
4,4'-DDT	5	3.1	61
	10	3.7	37
	20	14.0	71
	50	35.0	70
	100	77.0	77

Table 4 - Replicate 4 Data

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
Lindane	5	4.2	84
	10	7.0	70
	20	12.0	62
	50	33.0	66
	100	73.0	73
Aldrin	5	2.8	55
	10	5.0	50
	20	8.8	44
	50	28.0	55
	100	63.0	63
4,4'-DDT	5	3.2	63
	10	4.7	47
	20	13.0	66
	50	33.0	65
	100	79.0	79

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